Amendment, Applicants have adopted the Examiner's suggestion and have corrected the non-conventional English spelling by replacing "hydrogenfluoride" with "hydrogen fluoride" thereby obviating the rejection to claims 5-8.

In addition, claims 4-5, 9 and 10 were rejected for reciting the term "organic solvent having a hetero atom". By this Amendment, Applicants have amended claims 4-5, 9 and 10 to now recite "an organic solvent comprising molecules having a hetero atom" to more clearly and succinctly recite Applicants' invention. Subject matter basis for this Amendment can be found in the specification as filed on page 7, line 14 to page 8, line 24. Further, Applicants submit that one of ordinary skill in the art would readily appreciate that the conventional term in the art, "hetero atom", refers to an odd or dissimilar atom in the ring of a heterocyclic compound (see **Attachment C** – definition of "hetero atom"). Therefore, Applicants respectfully submit that claims 4-5, 9 and 10 as amended are not indefinite and therefore respectfully request that the rejection to these claims under 35 U.S.C. § 112, second paragraph, be withdrawn.

Claims 1-4, 9, and 14-15 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Wojtczak et al US Pat. No. 6,280,651 (hereinafter "Wojtczak"). Applicants respectfully submit that Wojtczak is not prior art of the present application under 35 U.S.C. § 103(a). The present application has a priority date of November 24, 1998 corresponding to the priority Japanese Patent Application No. 1998-332767. Enclosed with this Amendment, Applicants have provided an English translation of that priority document. Wojtczak has a filing date of December 16, 1998 and an issue date of August 28, 2001. Therefore, Wojtczak is not prior art of the present application under

35 U.S.C. § 103(a). Therefore, Applicants respectfully request that the Examiner withdraw the rejection to claims 1-4, 9, and 14-15 as being unpatentable over Wojtczak.

Claims 1-5, 9-10 and 14-15 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Bowden et al US Pat. No. 5,320,709 (hereinafter "Bowden"). The Examiner asserts that Bowden discloses a process for wet etching a BPSG layer and a thermal SiO_2 layer using a solution comprised of 4% NH_4F, 96% polyhydric alcohol at a temperature of 20-40°C. Further, the Examiner asserts that the etch rate of the BPSG is 4 angstroms at 25°C and an etch rate of the thermal SiO_2 of 14 angstroms at 25°C (the Examiner citing Bowden, columns 2-4 and Figures 2-4).

The claimed invention is directed to an etching solution having a thermal oxide (THOX) film etch rate and boron phosphosilicate glass (BPSG) film etch rate at 25°C of 100 angstroms/mn or lower and a ratio of (BPSG etch rate)/(THOX etch rate) of 1.5 or lower.

Contrary to the Examiner's assertion, Bowden clearly fails to teach or suggest the claimed ratio of (BPSG etch rate) [divided by] (THOX etch rate) and therefore Bowden fails to make the claimed invention obvious. Contrary to the Examiner's assertion, Figure 2 in Bowden clearly discloses the etch rate of BPSG is 14 angstroms at 25°C, <u>not</u> 4 angstroms as alleged by the Examiner. Further, Figure 2 clearly shows the etch rate of the thermal SiO_2 is 4 angstroms at 25°C not 14. Using the clearly disclosed BPSG etch rate of 14 angstroms, the ratio of the (BPSG etch rate)/(THOX etch rate) at 25°C in Figure 2 is 3.5. In sharp contrast to that of Bowden, the claimed invention clearly recites a (BPSG etch rate)/(THOX etch rate) of 1.5 or lower.

Therefore, Bowden's ratio of 3.5 is outside of the scope of the claimed invention and consequently, Bowden fails to teach or suggest the claimed invention.

Moreover, in sharp contrast to the clear teaching of Bowden, the present invention enables THOX and BPSG to be etched at nearly the same rate (see page 10, lines 21-25 of the present specification). On the contrary, Bowden clearly teaches different etch rates and thus teaches away from nearly the same rates.

Based on the foregoing discussion, Applicants respectfully submit that claims 1-5, 9-10 and 14-15 are not made obvious by Bowden and therefore respectfully request that the rejection under 35 U.S.C. § 103(a) to these claims be withdrawn.

Applicants gratefully appreciate the Examiner's indication of allowable subject matter of claims 6-8 and 11-13. By this Amendment, Applicants submit that all prior rejections are overcome, and that all pending claims are now in condition for allowance.

In view of the foregoing, Applicants respectfully submit that the present application is in condition for immediate allowance, and such action is earnestly solicited.

Respectfully submitted,

LARSON & TAYLOR, PLC

November 14, 2002

B. Aaron Schulman
Registration No. 31877

1199 North Fairfax Street, Suite 900
Alexandria, Virginia 22314
(703) 739-4900

ATTACHMENT A

Marked Up Replacement Claims

Following herewith is a marked up copy of each rewritten claim.

4. (Amended) The etching solution according to claim 1 comprising at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom.

5. (Amended) The etching solution according to claim 1 comprising (i) ammonium hydrogen_fluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom, the water being contained in a concentration of 3% by weight or lower.

6. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen_fluoride, water and isopropyl alcohol, the water being contained in a concentration of 3% by weight or lower.

7. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen_fluoride, water and ethanol, the water being contained in a concentration of 3% by weight or lower.

8. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen fluoride, water and acetone, the water being contained in a concentration of 3% by weight or lower.

9. (Amended) The etching solution according to claim 1 comprising (i) ammonium fluoride and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom.

10. (Amended) The etching solution according to claim 1 comprising (i) ammonium fluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom, the water being contained in a concentration of 10% by weight or lower.

marked claims

ATTACHMENT B

Clean Replacement Claims

Following herewith is a clean copy of each claim which replaces each previous claim having the same number.

4. (Amended) The etching solution according to claim 1 comprising at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom.

A1

5. (Amended) The etching solution according to claim 1 comprising (i) ammonium hydrogen fluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom, the water being contained in a concentration of 3% by weight or lower.

6. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen fluoride, water and isopropyl alcohol, the water being contained in a concentration of 3% by weight or lower.

7. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen fluoride, water and ethanol, the water being contained in a concentration of 3% by weight or lower.

8. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen fluoride, water and acetone, the water being contained in a concentration of 3% by weight or lower.

9. (Amended) The etching solution according to claim 1 comprising (i) ammonium fluoride and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom.

A1 cont

10. (Amended) The etching solution according to claim 1 comprising (i) ammonium fluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom, the water being contained in a concentration of 10% by weight or lower.

clean claims

About A Dictionary of Science, Oxford University Press from Oxford University Press

adjacent entries

Hertzsprung-Russell diagram (H-R diagram)
hesperidium
Hess's law
hetero atom
heterochromatin
heterocyclic
heterodont

hetero atom

An odd atom in the ring of a heterocyclic compound. For instance, nitrogen is the h atom in pyridine.

ATTACHMENT C

VERIFICATION OF TRANSLATION

Re: JAPANESE PATENT APPLICATION NO. 1998-332767

I, Ikuko AIHARA, of Kitahama TNK Building, 7-1, Dosho-machi 1-chome, Chuo-ku, Osaka-shi, Osaka 541-0045, Japan hereby declare that I am the translator of the document attached and certify that the following is true translation to the best of my knowledge and belief.

Signature of translator Ikuko Aihara

Ikuko AIHARA

Dated this 31st day of October, 2002

[Document Name] Specification

[Title of the Invention] Etching solution

[Claims]

[Claim 1]

An etching solution having a thermal oxide (THOX) film etch rate and boron phosphosilicate glass (BPSG) film etch rate at 25°C of 100Å/min or lower and a ratio of (BPSG etch rate) / (THOX etch rate) of 1.5 or lower.

[Claim 2]

The etching solution according to claim 1 comprising at least one member selected from the group consisting of fluoride salts and bifluoride salts.

[Claim 3]

The etching solution according to claim 2, wherein the solvent of the etching solution has a relative dielectric constant of 35 or lower.

[Claim 4]

The etching solution according to claim 2 or claim 3 comprising at least one member selected from the group consisting of organic acids and organic solvents having hetero atom(s).

[Claim 5]

The etching solution according to claim 1 comprising ammonium hydrogenfluoride and water, and at least one member selected from the group consisting of

organic acids and organic solvents having hetero atoms, wherein the content of water is 3% by weight or lower.

[Claim 6]

The etching solution according to claim 1 comprising ammonium hydrogenfluoride, water and isopropyl alcohol, wherein the concentration of water is 3% by weight or lower.

[Claim 7]

The etching solution according to claim 1 comprising ammonium hydrogenfluoride, water, and ethanol, wherein the concentration of water is 3% by weight or lower.

[Claim 8]

The etching solution according to claim 1 comprising ammonium hydrogenfluoride, water and acetone, wherein the concentration of water is 3% by weight or lower.

[Claim 9]

The etching solution according to claim 1 comprising ammonium fluoride and at least one member selected from the group consisting of organic acids and organic solvents having hetero atom(s).

[Claim 10]

The etching solution according to claim 1 comprising ammonium fluoride, water, and at least one member selected from the group consisting of organic acids

and organic solvents having hetero atoms, wherein the concentration of water is 10% by weight or lower.

[Claim 11]

The etching solution according to claim 1 comprising ammonium fluoride, water and ethanol, wherein the concentration of water is 10% by weight or lower.

[Claim 12]

The etching solution according to claim 1 comprising ammonium fluoride, water and isopropyl alcohol, wherein the concentration of water is 10% by weight or lower.

[Claim 13]

The etching solution according to claim 1 comprising ammonium fluoride, water and acetic acid, wherein the concentration of water is 1.5% by weight or lower.

[Claim 14]

A method for producing an etched article by etching an article with the etching solution as defined in any of claims 1-13.

[Claim 15]

An etched article which is produced by the method of claim 14.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to an etching solution, a method for producing an etched article and an etched article produced by the method, more specifically, to an etching solution etching doped oxide films such as boron phosphosilicate glass (BPSG) film and undoped oxide films such as thermal oxide (THOX) film at the same etch rate or similar etch rate, a method for producing an etched article, and an etched article produced by the method.

[0002]

[Prior Art and Problem to be Solved by the Invention]

Conventionally, as etchants for silicon wafers and the like, buffered hydrofluoric acids have been used which comprise HF (50-wt.% aqueous solution) and NH_4F (40-wt.% aqueous solution) mixed in a ratio capable of achieving a desired etch rate.

[0003]

However, the buffered hydrofluoric acids etch doped oxide films such as BSG (boron silicate glass film), BPSG, PSG (phosphosilicate glass film), AsSg (phosphosilicate glass film) and the like faster than they etch undoped oxide films such as TEOS (oxide film formed by CVD method using tetraethoxysilane gas) and like USG, THOX and the like. Therefore, the buffered hydrofluoric acids can not etch the doped oxide films and

undoped oxide films at the same rate.

[0004]

An object of the present invention is to provide an etching solution and an etching method for etching undoped oxide films such as TEOS, THOX and the like and oxide films doped with impurities at the same rate.

[0005]

[Means for Solving the Problem]

The present invention relates to the items 1-15 listed below.

Item 1. An etching solution having a thermal oxide (THOX) film etch rate and boron phosphosilicate glass (BPSG) film etch rate at 25°C of 100Å/min or lower and a ratio of (BPSG etch rate) / (THOX etch rate) of 1.5 or lower.

Item 2. The etching solution according to item 1 comprising at least one member selected from the group consisting of fluoride salts and bifluoride salts.

Item 3. The etching solution according to item 2, wherein the solvent of the etching solution has a relative dielectric constant of 35 or lower.

Item 4. The etching solution according to item 2 or 3 comprising at least one member selected from the group consisting of organic acids and organic solvents having hetero atoms.

Item 5. The etching solution according to item 1

comprising ammonium hydrogenfluoride and water, further comprising at least one member selected from the group consisting of organic acids and organic solvents having hetero atoms, wherein the concentration of water is 3% by weight or lower.

Item 6. The etching solution according to item 1 comprising ammonium hydrogenfluoride, water and isopropyl alcohol, wherein the concentration of water is 3% by weight or lower.

Item 7. The etching solution according to item 1 comprising ammonium hydrogenfluoride, water and ethanol, wherein the concentration of water is 3% by weight or lower.

Item 8. The etching solution according to item 1 comprising ammonium hydrogenfluoride, water and acetone, wherein the concentration of water is 3% by weight or lower.

Item 9. The etching solution according to item 1 comprising ammonium fluoride and at least one member selected from the group consisting of organic acids and organic solvents having hetero atom(s).

Item 10. The etching solution according to item 1 comprising ammonium fluoride, water and further comprising at least one member selected from the group consisting of organic acids and organic solvents having hetero atoms, wherein the concentration of water is 10% by weight or

lower.

Item 11. The etching solution according to item 1 comprising ammonium fluoride, water and ethanol, wherein the concentration of water is 10% by weight or lower.

Item 12. The etching solution according to item 1 comprising ammonium fluoride, water and isopropyl alcohol, wherein the concentration of water is 10% by weight or lower.

Item 13. The etching solution according to item 1 comprising ammonium fluoride, water and acetic acids, wherein the concentration of water is 1.5% by weight or lower.

Item 14. A method for producing an etched article by etching an article with the etching solution as defined in any of items 1-13.

Item 15. An etched article which is produced by the method of item 14.

[0006]

[Mode for Carrying out the Invention]

The etching solution of the present invention has the ratio of BPSG etch rate / THOX etch rate at 25°C of 1.5 or lower, preferably 1.3 or lower, more preferably 1.2 or lower, still more preferably 1.1 or lower, particularly 1.05 or lower.

[0007]

The BPSG is used for measuring etch rate after

being formed as a film and annealed.

[0008]

The etching solution of the present invention satisfies the above ratio of the etch rates, and also has a THOX etch rate and a BPSG etch rate at 25°C of 100Å/min or lower, preferably 80Å/min or lower, still more preferably 60Å/min or lower, particularly 50Å/min or lower.

[0009]

The etch rate of the etching solution of the invention can be determined by etching BPSG and THOX with the etching solution at 25°C and dividing the difference in the film thickness before and after being etched by the etch time.

[0010]

Examples the fluoride salts and bifluoride salts of the present invention include metal salts, ammonium salts and quaternary ammonium salts. Preferable examples of the metal salts include those which have high solubility, such as potassium fluoride, sodium fluoride, potassium hydrogenfluoride, sodium hydrogenfluoride and the like. Examples of the ammonium salts include ammonium fluoride and ammonium hydrogenfluoride (ammonium monohydrogendifluoride). Examples of the quaternary ammonium salts include tetramethylammonium fluoride, methylamine hydrofluoride, 2-hydroxyethyltrimethyl-

ammonium fluoride, tetramethylammonium hydrogenfluoride and the like.

[0011]

In the present invention, the relative dielectric constant is that of the solvent (an organic solvent having hetero atom(s), an organic acid or water) measured at 25° C.

[0012]

The relative dielectric constant is usually 35 or lower, preferably 25 or lower, more preferably 21 or lower.

[0013]

Ammonium monohydrogendifluoride to be used in the etching solution of the invention may be in the form of crystals or an aqueous solution. Alternatively, stoichiometric amounts of ammonium fluoride and HF may be added to the solvent to form ammonium hydrogenfluoride in the solution.

[0014]

The ammonium fluoride to be usd in the etching solution of the invention may be in the form of crystals or an aqueous solution.

[0015]

Examples of the organic acids include acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, caproic acid, caprylic acid,

monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monofluoroacetic acid, difluoroacetic acid, trifluoroacetic acid, á-chlorobutyric acid, â-chlorobutyric acid, γ-chlorobutyric acid, lactic acid, glycolic acid, pyruvic acid, glyoxalic acid, acrylic acid and like monocarboxylic acids, methanesulfonic acid, toluenesulfonic acid and like sulfonic acids, oxalic acid, succinic acid, adipic acid, tartaric acid, citric acid and like polycarboxylic acids.

[0016]

Examples of the organic solvents having hetero atoms include methanol, ethanol, isopropyl alcohol (IPA), 1-propanol, 1-butanol, 2-butanol, t-butanol, 2-methyl-1-propanol, 1-pentanol, 1-hexanol, 1-heptanol, 4-heptanol, 1-octanol, 1-nonylalcohol, 1-decanol, 1-dodecanol and like alcohols; ethylene glycol, 1,2-propanediol, propylene glycol, 2,3-butanediol, glycerin and like polyols, acetone, acetylacetone, methyl ethyl ketone and like ketones; acetonitrile, propionitrile, butyronitrile, isobutyronitrile, benzonitrile and like nitriles; formaldehyde, acetaldehyde, propionaldehyde and like aldehydes; ethylene glycol monomethyl ether, ethylene glycol monoethyl ether and like alkylene glycol monoalkyl ethers; tetrahydrofuran, dioxane and like ethers, trifluoroethanol, pentafluoropropanol, 2,2,3,3-tetrafluoropropanol and like fluorinated alcohols,

sulfolane, nitromethane and the like.

[0017]

The content of ammonium monohydrogendifluoride is about 0.01-5% by weight, preferably about 0.01-2.5% by weight.

[0018]

The content of ammonium fluoride is preferably about 0.01-4% by weight, more preferably about 0.01-2% by weight.

[0019]

The water content is preferably 10% by weight or lower, more preferably about 3% by weight or lower.

[0020]

The content of the organic acid is preferably 95% by weight or higher, more preferably 96% by weight or higher.

[0021]

The content of the organic solvent having hetero atom(s) is preferably 85% by weight or higher, more preferably 95% by weight or higher.

[0022]

Preferable etching solutions of the present invention and their compositions are shown below.

- Ammonium monohydrogendifluoride : IPA : water = 0.01-5% by weight : 92-99.99% by weight : 0-3% by weight;
- Ammonium monohydrogendifluoride : ethanol : water =

0.01-5% by weight : 92-99.99% by weight : 0-3% by weight;

- Ammonium monohydrogendifluoride : acetone : water = 0.01-5% by weight : 92-99.99% by weight : 0-3% by weight;
- Ammonium fluoride : IPA : water = 0.01-4% by weight : 86-99.99% by weight : 0-10% by weight;
- Ammonium fluoride : acetic acid : water = 0.01-4% by weight : 94.5-99.99% by weight : 0-1.5% by weight;
- Ammonium fluoride : ethanol : water = 0.01-5% by weight : 86-99.99% by weight : 0-10% by weight.

[0023]

The etching solution of the invention can be suitably used for etching articles having oxide films doped with B, P, As and the like (BSG, BPSG, PSG, AsSG, etc.) and an undoped oxide films including USG such as THOX, TEOS and the like.

[0024]

In the etching method of the present invention, the temperature of the etching solution is about 15-40°C, and the etch time is about 0.25-10 minutes.

[0025]

Examples of the articles to be etched are single crystalline silicon wafers, gallium-arsenic wafers and like wafers, preferably articles comprising a doped oxide film (BSG, BPSG, PSG, AsSG, etc.) and an undoped oxide film (THOX, TEOS and like USG).

[0026]

[Effect of the Invention]

The present invention provides an etching solution and a method for producing an etched article capable of etching THOX, TEOS and like USG and an oxide film doped with impurities, such as BPSG, BSG and the like at nearly the same rate, and an etched article produced by the method.

[0027]

[Examples]

The present invention will be explained in more detail referring to Examples and Comparative Examples given below.

[0028]

Hereinafter, the relative dielectric constant is that of the solvent (an organic solvent having a hetero atom, an organic acid or water) at 25°C.

[0029]

The etch rate was determined by measuring the thickness of the films before and after the etching using Auto EL-III ellipsometer manufactured by Rudolf Research.

[0030]

The etch rate of the etching solution was calculated by etching each film with the etching solution at 25°C and dividing the difference in the film thickness before and after being etched by the etch time.

Examples 1-3 and Comparative Examples 1-2

Ammonium monohydrogendifluoride ($NH_4F \cdot HF$), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 1. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and etch selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon.

[0031]

The results are shown in Table 1.

[0032]

Table 1

Ammonium monohydrogendifluoride/organic solvent/water etching solution

	Organic solvent	Relative dielectric constant	$NH_4F \cdot HF$ concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 1	IPA	19.9	2.28	96.22	1.5	58	52	0.90
Ex. 2	Acetone	20.7	2.28	96.22	1.5	16	18	1.13
Ex. 3	Ethanol	24.6	2.28	96.22	1.5	31	37	1.19
Comp. Ex. 1	Ethanol	32.7	2.28	96.22	1.5	63	120	1.90
Comp. Ex. 2	(Water)	78.3	2.28	0	97.72	44	358	8.14

Examples 4-7 and Comparative Example 3

Ammonium fluoride (NH_4F), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 2. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 2.

[0033]

Table 2

Ammonium fluoride/organic solvent/water etching solution

	Organic solvent	Relative dielectric constant	NH_4F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 4	Acetic acid	6.2	1.85	98.15	0	77	70	0.91
Ex. 5	IPA	19.9	1.48	93.52	5.0	8	10	1.25
Ex. 6	Ethanol	24.6	1.48	93.52	5.0	11	15	1.36
Ex. 7	Ethanol	32.7	1.47	97.02	1.5	8	11	1.38
Comp. Ex. 3	(Water)	78.3	1.48	0	98.52	<3	<3	--

Example 8 and Comparative Examples 4-7

Ammonium monohydrogendifluoride ($NH_4F \cdot HF$), ammonium fluoride (NH_4F), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 3. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 3.

[0034]

Table 3

Ammonium monohydrogenbifluoride/ammonium fluoride/organic solvent/water etching solution

	Organic solvent	Relative dielectric constant	$NH_4F \cdot HF$ concentration (%)	NH_4F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 8	Ethanol	24.6	0.7125	1.48	92.81	5.0	28	35	1.25
Comp. Ex. 4	(Water)	78.3	0.7125	9.5375	0	89.75	59	163	2.76
Comp. Ex. 5	(Water)	78.3	0.7125	19.5375	0	79.75	63	153	2.43
Comp. Ex. 6	(Water)	78.3	0.7125	29.5375	0	69.75	59	107	1.81
Comp. Ex. 7	(Water)	78.3	0.7125	39.5375	0	59.75	43	66	1.53

Examples 9-13 and Comparative Example 8

Ammonium monohydrogenbifluoride ($NH_4F \cdot HF$), water and IPA were mixed at the ratios shown in Table 4. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 4.

[0035]

Table 4

Ammonium monohydrogenbifluoride/2-propanol/organic solvent/water etching solution

	Organic solvent	Relative dielectric constant	$NH_4F \cdot HF$ concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 9	IPA	19.9	0.1425	98.8575	1.0	19	18	0.95
Ex. 10	IPA	19.9	0.1425	98.3575	1.5	12	13	1.08
Ex. 11	IPA	19.9	0.1425	97.8575	2.0	17	23	1.35
Ex. 12	IPA	19.9	0.1425	97.3575	2.5	24	33	1.38
Ex. 13	IPA	19.9	0.1425	96.8575	3.0	24	36	1.50
Comp. Ex. 8	IPA	19.9	0.1425	94.3575	5.0	23	43	1.87

Examples 14-15 and Comparative Examples 9-10

Ammonium fluoride (NH_4F), water and ethanol were mixed at the ratios shown in Table 5. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 5.

[0036]

Table 5

Ammonium fluoride/ethanol/water etching solution

	Organic solvent	Relative dielectric constant	NH_4F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 14	Ethanol	24.6	1.48	97.02	1.5	8	10	1.25
Ex. 15	Ethanol	24.6	1.48	88.52	10.0	13	18	1.38
Comp. Ex. 9	Ethanol	24.6	1.48	83.52	15.0	12	29	2.42
Comp. Ex. 10	Ethanol	24.6	1.48	68.52	30.0	<3	27	--

Examples 16-19 and Comparative Examples 11-12

Ammonium fluoride (NH_4F), water and acetic acid were mixed at the ratios shown in Table 6. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 6.

[0037]

Table 6

Ammonium fluoride/acetic acid/water etching solution

	Organic solvent	Relative dielectric constant	NH_4F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 16	Acetic acid	6.2	0.2775	99.7225	0	27	38	1.41
Ex. 17	Acetic acid	6.2	0.37	99.63	0	72	67	0.93
Ex. 18	Acetic acid	6.2	0.37	96.3	1.0	73	95	1.31
Ex. 19	Acetic acid	6.2	0.925	99.075	0	73	69	0.95
Comp. Ex. 11	Acetic acid	6.2	3.7	96.3	0	104	101	0.97
Comp. Ex. 12	Acetic acid	6.2	0.37	96.3	3.0	75	154	2.05

Example 20 and Comparative Examples 13-14

Ammonium monohydrogenbifluoride ($NH_4F \cdot HF$), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 7. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using test substrates each comprising a silicon substrate and one of undoped oxide films (THOX, TEOS) and doped oxide films (BSG, BPSG, PSG, AsSG) formed thereon. The results are shown in Table 7.

[0038]

Table 7

Etch rates of doped films and undoped films

	Ex. 20	Comp. Ex. 13	Comp. Ex. 14
Organic solvent	IPA	(Water)	(Water)
Relative dielectric constant	19.9	78.3	78.3
$NH_4F \cdot HF$ concentration (%)	0.57	0.57	0.7125
NH_4F concentration (%)	0	0	39.5375
Organic solvent concentration (%)	98.675	0	0
Water concentration (%)	0.755	99.43	59.75
Etch rate			
THOX etch rate (Å/min.)	38	22	43
TEOS etch rate (Å/min.)	47	39	61
BSG etch rate (Å/min.)	48	171	93
BPSG etch rate (Å/min.)	39	179	66
PSG etch rate (Å/min.)	43	63	75
AsSG etch rate (Å/min.)	40	174	120
Etch rate selectivity			
TEOS/THOX	1.24	1.77	1.42
BSG/THOX	1.26	7.77	2.16
BPSG/THOX	1.03	8.14	1.53
PSG/THOX	1.13	2.86	1.74
AsSG/THOX	1.05	7.91	2.79

[Document Name] Abstract

[Abstract]

[Object]

An object of the present invention is to provide a composition for etching doped and undoped oxide films at the same rate.

[Method for Achieving the Object]

An etching solution having a thermal oxide (THOX) film etch rate and a boron phosphosilicate glass (BPSG) film etch rate at 25°C of 100Å/min or lower and the ratio of (BPSG etch rate) / (THOX etch rate) of 1.5 or lower.

[Selected Figure] Not present